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☐ Additional inventors are being named on the _____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

A Solvent-Resistant Photocured Perfluoropolyether-Based Microfluidic Device

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ENCLOSED APPLICATION PARTS (check all that apply)

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☐ Application Data Sheet. See 37 CFR 1.76

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A Solvent-Resistant Photocured Perfluoropolyether-Based Microfluidic Device

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Microfluidic devices first developed in the early 1990s were fabricated from silicon and glass using photolithography and etching techniques.^{1,2} These processes were costly, required clean-room conditions, were labor intensive, and posed several disadvantages from a materials standpoint. The fabrication of valves in hard materials is difficult and requires increasing the area of the device.² Furthermore, it is often necessary to bond two layers of a device together. This is achieved only at very high temperatures with silicon and glass.² For these reasons, soft materials have emerged as excellent alternatives for microfluidic device fabrication. Soft materials make possible the easy manufacture and actuation of devices containing valves, pumps, and mixers¹⁻⁵ This has allowed microfluidics to explode into a ubiquitous technology that has found application in genome mapping, rapid separations, sensors, nano-scale reactions, ink-jet printing, and drug screening.¹⁻⁶

Poly(dimethylsiloxane) (PDMS) has served as the material of choice for virtually all recent microfluidic device fabrication.²⁻⁶ PDMS offers numerous attractive properties in relation to microfluidics. Upon crosslinking, it becomes an elastomeric material with a low Young's modulus of ~750 kPa.³ This enables it to conform to surfaces and form reversible seals. It has a low surface energy usually around 20 erg/cm² which facilitates easy release from molds after patterning.^{2,4} Another important feature of PDMS is its outstanding gas permeability. This allows for gas bubbles within channels to permeate out of the device and is also useful in sustaining cells and microorganisms inside the features. The nontoxic nature of silicones is also beneficial in this respect and allows for opportunities in the realm of medical implants.⁴

Most current PDMS devices are based on Sylgard 184[®] (Dow Corning) which cures thermally through a platinum-catalyzed hydrosilation reaction. With this material, complete curing can take up to 5 hours. To expedite this process, Rogers *et al.* have recently reported the synthesis of a photocurable PDMS material with mechanical properties similar to that of Sylgard 184[®] for use in soft lithography.⁷ This material cures through the use of free radical photoinitiators in just a few minutes.

Despite the advantages of PDMS in relation to microfluidics technology, the material suffers from a serious drawback in that it swells in most organic solvents. Whitesides *et al.* have recently reported in detail on the limited compatibility of PDMS-based microfluidic devices with various organic solvents.⁸ Among those that greatly swell the material are hexanes, ethyl ether, toluene, methylene chloride, acetone, and acetonitrile.⁸ The swelling of PDMS-based devices in organic solvents greatly disrupts the micron-sized features and makes it impossible for fluids to flow inside the channels. For this reason, it might be said that the field of microfluidics has largely been restricted to aqueous-based

applications. As a solution to the swelling problem, Whitesides has proposed that those applications requiring the use of organic solvents will need to revert back to first-generation systems using glass and silicon.⁸ However, this approach is greatly limited by the disadvantages outlined earlier.

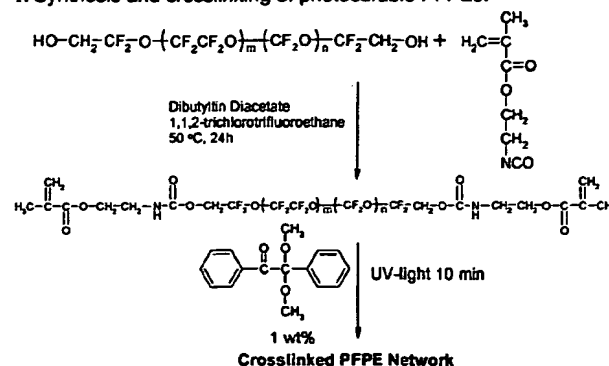
Thus, an elastomer which exhibits the attractive properties of PDMS along with a resistance to swelling in common organic solvents would greatly extend the use of microfluidic devices to a wide variety of new chemical applications and other domains yet to be explored. With the added advantage of photocuring capability, the production time of microfluidic devices can be reduced from several hours to a matter of minutes.

Our approach to this problem has been to replace PDMS with perfluoropolyethers (PFPEs). PFPEs are a unique class of fluoropolymers that exhibit low surface energy, low modulus, high gas permeability, and low toxicity with the added feature of being extremely chemically resistant.⁹ DeSimone *et al.* have reported extensively on the synthesis and solubility of PFPEs in supercritical carbon dioxide.¹⁰ Herein we report the first fabrication of a microfluidic device based on photocurable PFPEs.

Materials Synthesis and Characterization

The synthesis and photocuring of these materials (Scheme 1) is based on earlier work done by Bongiovanni *et al.*¹¹ The reaction involves the methacrylate-functionalization of a commercially available PFPE diol ($M_n = 3,800$ g/mol) with isocyanato-ethyl methacrylate. Subsequent photocuring of the material is accomplished by blending it with 1 wt% of 2,2-dimethoxy-2-phenylacetophenone (DMPA) and exposing it to UV radiation ($\lambda = 365$ nm).

To measure solvent resistance, tests using classical swelling measurements¹² were performed on both the crosslinked PFPE DMA and Sylgard 184[®]. Sample weight was compared before and after immersion in dichloromethane for several hours. The Scheme 1. Synthesis and crosslinking of photocurable PFPEs.



data show that after 94 h the PDMS network had swelled to 109% by weight, while the PFPE network showed negligible swelling (< 3%)

The PDMS and PFPE precursor materials and the fully cured networks have similar processing and mechanical properties (insert Viscosity data here). Dynamic mechanical thermal analysis was performed on the fully cured materials. Both the PFPE and PDMS networks exhibited low-temperature transitions (-112 °C and -128 °C respectively) as evidenced by maxima in the loss modulus E'' (Figure 1). This transition accounts for the similar elastic behavior of the two crosslinked materials at room temperature.

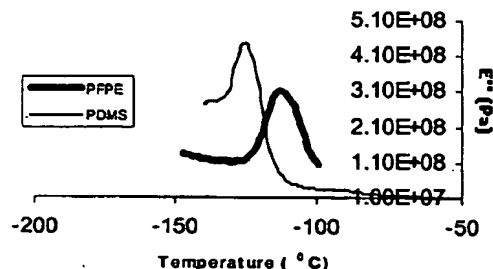


Figure 1. DMTA traces of crosslinked PDMS and PFPE materials showing maxima in the storage modulus as a function of temperature.

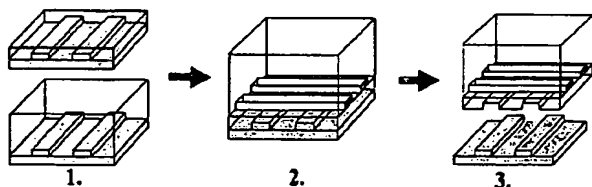


Figure 2. Device fabrication procedure. 1.) A small drop of PFPE DMA containing 1wt% DMPA was spin coated onto a patterned silicon wafer to a height of 20 μm . Separately, a thicker layer (~5 mm) is formed by pouring PFPE DMA containing 1 wt% DMPA into a mold surrounding a patterned wafer. Both wafers are then exposed to UV light for 30 s. 2.) The thick layer is peeled off its wafer, rotated 90°, and placed on top of the thin layer. The entire device is then exposed to UV light for 10 min. to adhere the two layers together. 3.) The device is peeled off the wafer.

Device Fabrication

Device fabrication was accomplished according to the procedure illustrated in Figure 2. This method was first reported by Quake *et al.* for PDMS devices and utilizes partial curing techniques to adhere the two layers without compromising feature sizes.³ The PFPE DMA material was easily spin-coated and molded in the same manner as procedures using Sylgard 184®. Channels in the thick layer were 50 μm X 100 μm while channels in the thin layer were 12 μm X 100 μm .

To compare the solvent compatibility of devices made from the two materials, a dyed solution containing dichloromethane, acetonitrile, and methanol was introduced into both a PFPE and a PDMS channel by capillary action (Figure 3). The PFPE channels showed no evidence of swelling as the solution traveled easily through the channel. A pronounced reverse meniscus was observed indicating good wetting behavior. In contrast, no solution was able to be processed in the PDMS device because the channel was visibly swelled shut when it made contact with the droplet. As a control, a dyed methanol solution was easily introduced in the PDMS channel in the same manner.

Actuation of the valves was accomplished by introducing slightly pressurized air (~25 psi) to small holes that were punched through the thick layer at the beginning of the channels.

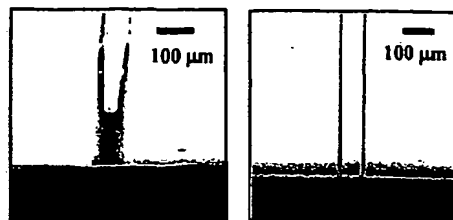


Figure 3. Dyed solution of methylene chloride, acetonitrile, and methanol entering PFPE device channel (left). No solution entered a PDMS channel of the same size due to swelling (right).

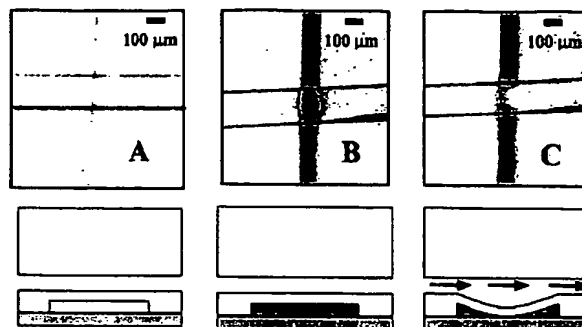


Figure 4. A.) Top-down view of channels containing no solvent. The channels on the thin layer run vertical, while those on the thick layer run horizontal. B.) Thin layer channel filled with dyed solution of acetonitrile, dichloromethane, and methanol. C.) Valve actuation produced by introducing 20 psi of air into the thick layer channel. Beneath each picture, a cartoon representation of the valve cross-section is shown.

When the solution was present in the channel, valve actuation was easily observed (Figure 4).

To summarize, we have presented a novel solvent-resistant microfluidic device fabricated from PFPE-based elastomers. Device formation and valve actuation were accomplished using established procedures for PDMS devices. Photocuring allows fabrication time to be decreased from several hours to a matter of minutes. The PFPE-based device showed a remarkable resistance to organic solvents. This work has the potential to expand the field of microfluidics to novel applications. Current efforts to use a PFPE-based device in a novel approach to DNA synthesis are underway.

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